

REMARKS

The Office Action raised an issue with regards to Claim 2 under 35 U.S.C. §112, which is now mooted by our amendments.

The present invention is assigned to Matsushita Electrical Industrial Company, that manufactures a line of Plasma Display Panels (PDP) under the mark PANASONIC.

As the Patent Office is aware, this is a highly competitive field with relatively large international companies utilizing scientists and engineers to seek improvements in performance, production, efficiency and cost. As the size of plasma display panels have become larger and less expensive, more competitive issues are presented in a challenging economic environment.

As can be appreciated from our current specification, there is a balance that must be achieved in maintaining illumination efficiency in PDPs while reducing power requirements for charging a protective layer in individual cells while ensuring that there is not a discharge delay, black noise, erosion of the protective layer by ion sputtering, contamination, and maintaining an adequate secondary electron emission efficiency.

Within this crowded field, the present invention is believed to offer a unique improvement which should be taken into consideration when judging the patentability of our current claims.

"Thus when differences that may appear technologically minor nonetheless have a practical impact, particularly in a crowded field, the decision-maker must consider the obviousness of the new structure in this light."

Continental Can Co. USA Inc. v. Monsanto Co., 20 U.S.P.Q. 2d. 1746, 1752 (Fed. Cir. 1991).

As noted in our description of the prior art in our specification, conventional technology has attempted to improve an electron emission factor and to restrict a discharge delay by adding

selected impurity elements into the protective layer. Consequences, however, have included limiting the wall charge retaining power so that it is difficult to generate an adequate discharge.

Our claims, as presented with this Amendment, provide a dielectric layer and a protective layer formed on a substrate wherein the protective layer contains a specific effective amount of Ge in a range of 10 mass ppm to 30 mass ppm, inclusive, and further contains H in a range of 1000 mass ppm to 2000 mass ppm, inclusive, with respect to the MgO content of the protective layer. With this arrangement, an image display quality in the gas discharge panel can be improved and the problem of discharge delay can be solved while maintaining a desired wall charge to facilitate secondary electron emission from the protective layer. This is also accomplished while reducing a discharge starting voltage and lowering both power consumption and the heat generated by larger display panels.

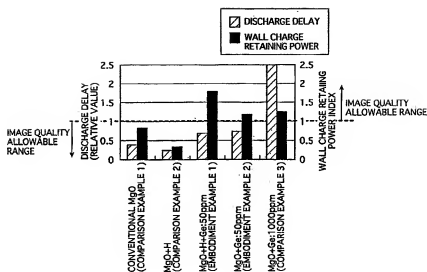
Support for the amendment to Claim 1 can be found as follows:

[0034] Furthermore, a structure is also possible in which the protective layer contains H and Ge in addition MgO, where the Ge content is in a range of 10 mass ppm to 300 mass ppm inclusive with respect to the MgO content.

[0150] The result further shows that if the H content is in the range of 1000 mass ppm to 2000 mass ppm inclusive, it is preferable since the effect of restraining discharge delay occurrence is particularly obtainable.

Applicant also provides, in Figure 5, a graph showing a comparison of the protective layer discharge delay in relative value and also a wall charge retaining power index. See Paragraph 0085. Attention is directed specifically to the embodiment of Example 1 wherein the MgO content of the protective layer is supplemented with Hydrogen and Germanium.

As can be seen in Figure 5, the embodiment now defined by our claims discloses that the wall charge retaining power index is greater than 1, while the discharge delay is less than 1.



Our amended Claim 2 is further supported by our specification in Paragraph 0147 as follows:

[0147] Furthermore, if the Ge content is within the range of 20 mass ppm to 100 mass ppm inclusive, it is confirmed that the image display quality is particularly excellent.

The Office Action had rejected Claims 1, 2, 5, 8 and 9 as being completely anticipated by *Ito et al.* (Patent Abstracts of Japan Publication 2002/033053).

“An anticipating reference must describe the patented subject matter with sufficient clarity and detail to establish that the subject matter existed in the prior art and that such existence would be recognized by persons of ordinary skill in the field of the invention.” See *In re Spada*, 911 F.2d 705, 708, 15 USPQ2d 1655, 1657 (Fed. Cir. 1990); *Diversitech Corp. v. Century Steps, Inc.*, 850 F.2d 675, 678, 7 USPQ2d 1315, 1317 (Fed. Cir. 1988).

The Office Action specifically contended the *Ito et al.* reference taught infusion of H in a range of 300 mass ppm to 10000 mass ppm inclusive, with regards to the MgO content of the protective layer.

Actually *Ito et al.* teaches the following:

[0071] Therefore, a hydrogen content shall be three atoms or more, when the number of the atoms of the whole protective film is set to 100.

[0072] However, since the defect in a protective film and the content of magnesium hydroxide will increase and the sputtering-proof nature as a protective film will fall, if it exceeds ten atom when a hydrogen content sets the number of the atoms of the whole protective film to 100, As for a hydrogen content, when the number of the atoms of the whole protective film is set to 100, it is preferred that it is ten atom or less. (underline added)

Ito et al. discloses that a protective film for a gas discharge panel should contain 3 hydrogen atoms to 10 hydrogen atoms inclusive when the number of total atoms in the protective film is defined as 100 (see, for example, Paragraphs 0071 and 0072). Since the protective film of *Ito et al.* is made of MgO, it contains equivalent numbers of atoms of Mg and O. In other words, in the case of the protective film disclosed in *Ito et al.*, the protective film should contain H atoms in a range of 1544 mass ppm to 5527 mass ppm inclusive with respect to a MgO content of the protective film.

Ito et al. neither discloses nor suggests adding any relative predetermined amounts of Ge and H to a protective layer which is mainly composed of MgO, as recited in Claim 1 after amendment of the present application. *Ito et al.* merely discloses a gas discharge panel in which a protective film contains H atoms in a range of 1544 mass ppm to 5527 mass ppm inclusive.

To assist the Examiner, enclosed is an English translation not only of the Patent Abstract, but also of a detailed description that we were able to find online for the *Ito et al.* application.

The Office Action had also rejected Claims 3, 4, 7, 10 and 11 as being obvious under 35 U.S.C. §103 over a combination of the *Ito et al.* reference when further taken in view of *Hasegawa et al.* (Patent Abstract, Japanese Patent Publication 2004-031264). This reference is also assigned to the present applicant.

The Office Action contended that incorporating Si into a protective layer of MgO in a range of 20 mass ppm to 5000 mass ppm, was appropriate to prevent an absorption of carbon dioxide and water into the protective layer. Actually, the reference suggests silicon of 500 to 15000 wt per ppm could be added, along with Ge having a range of 300 to 8000 wt ppm.

A person of ordinary skill in the field would find that the teaching of the *Hasegawa et al.* reference, would require both Silicon and Germanium to be utilized with the understanding that the Silicon would create a surface barrier film on the MgO such as Mg_2SiO_4 , or $MgSiO_3$ to prevent absorption of carbon dioxide or water. Additionally, it would purportedly prevent impurity gas from being released into the protective layer. See Paragraph 0009 of the *Hasegawa et al.* specification.

There is no suggestion nor teaching, however, of a ratio between Hydrogen and Germanium as defined in our current claims that would produce the advantageous result as shown, for example, in our Figure 5.

In essence, the Office Action utilizes, in a piecemeal manner, selected portions from the *Ito et al.* reference in combination with limited portions from the *Hasegawa et al.* reference. As set forth in the Manual of Patent Examination Procedure, each of the references must be considered in their entirety.

A prior art reference must be considered in its entirety, i.e., as a whole, including portions that would be lead away from the claimed invention. *W.L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983), *cert. denied*, 469 U.S. 851 (1984).

MPEP 2141.02 VI

Our recent discussion with Pinchus Laufer in the Office of Patent Legal Administration, who was involved in writing the Examination Guidelines for Determining Obviousness under 35 USC §103 in view of the Supreme Court decision in *KSR International Co. vs. Teleflex, Inc.*

verified that the KSR decision still required a specific rationale that could not be based on hindsight for purportedly combining the elements in the prior art to meet an invention defined in the patent claims.

Mr. Laufer incorporated the following from the existing MPEP into the Guidelines.

As noted in the MPEP at §2143.02:

A rationale to support a conclusion that a claim would have been obvious is that all the claimed elements were known in the prior art and one skilled in the art could have combined the elements as claimed by known methods with no change in their respective functions, and the combination would have yielded nothing more than predictable results to one of ordinary skill in the art., *KSR International Co. v. Teleflex Inc.*, 550 U.S. ___, ___, 82 USPQ2d 1385, 1395 (2007); *Sakraida v. AG Pro, Inc.*, 425 U.S. 273, 282, 189 USPQ 449, 453 (1976); *Anderson's-Black Rock, Inc. v. Pavement Salvage Co.*, 396 U.S. 57, 62-63, 163 USPQ 673, 675 (1969); *Great Atlantic & P. Tea Co. v. Supermarket Equipment Corp.*, 340 U.S. 147, 152, 87 USPQ 303, 306 (1950). (underline added)

Applicant respectfully submits that it is inappropriate to utilize applicant's own disclosure and in hindsight, select limited teachings in separate references, particularly when such teachings still do not define a combination of claim elements as now set forth in our amended claims.

As mentioned above, this is a relatively crowded field, yet important inventions can still be found that provide an advantage to the consumer in both increased performance, life of a PDP, and lower product cost.

Applicant, accordingly, requests reconsideration in view of the new claims and if the rejection is maintained over the current claims, a concise rationale as to why a person would have selected the specific values of Ge and Hydrogen, as set forth in our current claims, to achieve the advantageous effects of our present invention.

It is respectfully submitted that a person of ordinary skill would have, when subject to the broader teachings in these references, not have had an incentive to combine these two disclosures except in hindsight.

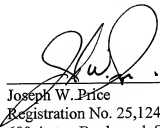
Finally, the ranges set forth in our current claims cannot be met by any combination of these two references.

It is believed the case is now in condition for allowance, and early notification of the same is requested.

If the Examiner believes that a telephone conference would assist in the prosecution of this matter, the undersigned attorney can be contacted at the listed telephone number.

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PATENT ABSTRACTS OF JAPAN

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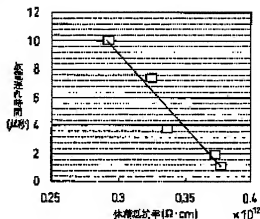
HIRANO TOSHIAKI

(54) PROTECTING FILM, METHOD OF FORMING THE SAME, PLASMA DISPLAY PANEL
AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a protecting film capable of improving the luminance, reducing the writing failure and reducing a driving circuit by shortening the discharge delay time while securing the sufficient sputtering resistance, and to provide a method of forming the protecting film and a method of manufacturing a plasma display panel.

SOLUTION: Discharge delay time is shortened with a rise of the volume resistivity. An allowable range of the discharge delay time depends on a PDP driving method and shape of a discharge cell. For example, when a discharge delay time exceeds about 4 μ seconds, scanning from both upper and lower ends of the PDP is required to secure the scanning time. Since it is necessary to set the scanning pulse width long, the number of maintaining pulse is limited, and it is hard to obtain the sufficient luminance. When the discharge delay time is less than



about 4 μ seconds, a sufficient scanning period can be secured by the scanning from one side, and the driving circuit can be reduced. Furthermore, since the scanning pulse having a width for requiring the limitation of the number of maintaining pulse is unnecessary, the sufficient luminance can be obtained.

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- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]A protective film which contains a metallic oxide in a protective film which protects a dielectric layer provided in a plasma display panel from discharge, and is characterized by volume resistivity being more than 3.5×10^{11} omega-cm.

[Claim 2]The protective film according to claim 1 containing three atoms or more of hydrogen atoms when the number of the whole atoms is set to 100.

[Claim 3]A protective film containing hydrogen from which the number of atoms when the number of a metallic oxide and the whole atoms is set to 100 becomes three or more in a protective film which protects a dielectric layer provided in a plasma display panel from discharge.

[Claim 4]A protective film given in any 1 paragraph of claims 1 thru/or 3, wherein said metallic oxide is MgO.

[Claim 5]The protective film according to claim 4 characterized by a peak of luminescence intensity of a luminescence center at 510 thru/or 560 nm being higher than a peak of luminescence intensity of a luminescence center at 280 thru/or 440 nm or 680 thru/or 760 nm in cathode luminescence.

[Claim 6]The protective film according to claim 5, wherein the number of said hydrogen atoms is more than the total number of deficits of the whole oxygen atom and a metal atom.

[Claim 7]A protective film given in any 1 paragraph of claims 1 thru/or 6 forming by heat-treating in atmosphere containing hydrogen of excitation or an ionization state.

[Claim 8]A protective film given in any 1 paragraph of claims 1 thru/or 7, wherein surface roughness Ra is not less than 5 nm.

[Claim 9](111) A protective film given in any 1 paragraph of claims 1 thru/or 8 by which orientation being shown.

[Claim 10]A method for film deposition of a protective film characterized by comprising the

following.

A process of forming a metal oxide film.

A process of heat-treating said metal oxide film in atmosphere containing hydrogen of excitation or an ionization state.

[Claim 11]A method for film deposition of a protective film having the process of forming a film which contains a metallic oxide while heat-treating in atmosphere containing hydrogen of excitation or an ionization state.

[Claim 12]A plasma display panel having a protective film of a statement in any 1 paragraph of claims 1 thru/or 9.

[Claim 13]A manufacturing method of a plasma display panel having the process of forming a protective film by a method according to claim 10 or 11.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the protective film which aimed at improvement in a discharge characteristic especially, its method for film deposition, a plasma display panel, and a manufacturing method for the same about a protective film suitable as a film which protects the dielectric layer of a plasma display from discharge, its method for film deposition, a plasma display panel, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]generally, a plasma display panel (PDP) does not have a flicker at thin structure, and it is comparatively alike, it can be considered [that a display contrast ratio is large and] as a big screen, and its speed of response is quick, and it has many features -- multicolor luminescence is also possible -- by use of a fluorescent substance with the spontaneous light type. For this reason, in the computer-related display field, the field of a color image display, etc., it is coming to use widely in recent years.

[0003]There are an alternating current drive type thing which an electrode is covered with a dielectric by that operation method, and is indirectly operated in the state of exchange discharge, and a direct-current drive type thing which an electrode is exposed to discharge space and operates in the state of direct current discharge in this plasma display. There are a memory operation type which uses the memory of a discharge cell as a drive system, and a refresh operation type which does not use it in an alternating current drive type plasma display. The luminosity of an alternating current drive type plasma display is proportional to discharge times. In the case of the above-mentioned refresh type, since luminosity will fall if display capacity becomes large, it is mainly used to the plasma display of small display capacity.

[0004]Drawing 16 is a typical exploded view showing the structure of a memory operation type alternating current drive type color plasma display.

[0005]The two insulating substrates 101 and 102 which consist of glass are formed in PDP. The insulating substrate 101 turns into a rear face substrate, and the insulating substrate 102 turns into a front substrate.

[0006]The transparent electrodes 103 and 104 are formed in the opposed face side with the insulating substrate 101 in the insulating substrate 102. The transparent electrodes 103 and 104 are prolonged to the horizontal direction (transverse direction) of the panel. The trace electrodes 105 and 106 are arranged so that it may lap with the transparent electrodes 103 and 104, respectively. The trace electrodes 105 and 106 are metal, for example.

It is provided in order to make small the electrode resistance value between each electrode and an external drive.

two or more black stripe layers 108 which are formed on the wrap dielectric layer 112 and the dielectric layer 112 in the transparent electrodes 103 and 104, and are prolonged to the perpendicular direction (lengthwise direction) of a panel and the red formed between this black stripe layer 108 -- (R). The protective film 114 which protects the color filter layers 110R, 110G, and 110B of green (G) and blue (B), the dielectric layer 112, and transparent electrode 103 grade from discharge is formed.

[0007]The emitted ultraviolet rays excite a fluorescent substance, PDP gives off each visible light of R, G, and B, and a color filter layer is necessarily unnecessary. It is for a color filter layer amending the spectrum of the luminescent color by a fluorescent substance.

[0008]The data electrode 107 which intersects perpendicularly with the transparent electrodes 103 and 104 is formed in the opposed face side with the insulating substrate 102 in the insulating substrate 101. Therefore, the data electrode 107 is prolonged perpendicularly. It is horizontal and the septum 109 which divides a display cell is formed. The septum 109 counters with the black stripe layer 108. The data electrode 107 is formed in the wrap dielectric layer 113, and the fluorescent substance layer 111 which changes into visible light the ultraviolet rays generated by discharge of discharge gas on the side of the septum 109 and the surface of the dielectric layer 113 is formed. And discharge gas space is secured in the space of the insulating substrates 101 and 102 by the septum 109, and it fills up with the discharge gas which consists of these mixed gas, such as helium, neon, or a xenon, in this discharge gas space.

[0009]As mentioned above, the protective film 114 is formed in order to protect the dielectric layer 112 and transparent electrode 103 grade from sputtering by the ion bombardment at the time of discharge.

Since the protective film 114 touches discharge gas space, the construction material and membraneous quality have big influence on a discharge characteristic.

In alternating current drive type PDP, low power consumption, the simplification of a drive circuit, highly-minute-izing, and big screen-ization serve as an important element.

[0010]For this reason, generally magnesium oxide (MgO) is used for the material of the protective film 114. It is because MgO is excellent in sputtering-proof nature and it is an insulating material with a large secondary electron emission factor. By using MgO, firing potential is dropped and the drive of PDP is attained.

[0011]Next, the method for film deposition of the protective film in PDP is explained. Generally the protective film is formed by the method of a vacuum deposition method. Drawing 17 is a mimetic diagram showing the film deposition system of the conventional protective film.

[0012]The vacuum evaporation chamber 121 is formed in the conventional film deposition system. The substrate 124 with which a dielectric film etc. are already formed and a MgO film is formed is attached to the upper part of the vacuum evaporation chamber 121. The deposition source 125 which consists of MgO(s) as a raw material of a protective film is attached to the lower part of the vacuum evaporation chamber 121. The gas inlet the heater 132 which heats the substrate 124, and for O₂ gas (not shown) is established in the vacuum evaporation chamber 121.

[0013]When manufacturing a protective film using the conventional film deposition system constituted in this way, first, fix the substrate 124 to the upper part of the vacuum evaporation chamber 121, and the substrate 124 is heated with the heater 132, and the inside of the vacuum evaporation chamber 121 is exhausted. Next, a MgO film is formed as a protective film by irradiating the deposition source 125 with the electron beam 133 on the field which counters the deposition source 125 of the substrate 124, introducing oxygen gas in the vacuum evaporation chamber 121, in order to arrange the crystal orientation of a MgO film.

[0014]In order to raise the stacking tendency of a MgO film, the method of forming a MgO film in the atmosphere containing the hydrogen atom of excitation or an ionization state is indicated (JP,9-295894,A).

[0015]Orientation of a protective film is made into (n00) or (mm0) orientation for the purpose of raising the secondary electron emission factor of a protective film, and falling discharge voltage, and PDP which set surface roughness to not less than 30 nm is indicated (JP,11-3665,A).

[0016]

[Problem(s) to be Solved by the Invention]It **, and in the display action of conventional memory operation type AC type PDP, first, a discharge voltage pulse is impressed to the transparent electrodes 103 and 104, and discharge is generated in discharge space. By this discharge, the electric charge which has the polarity impressed to each electrode and opposite polarity is accumulated in the portion which the transparent electrodes 103 and 104 meet on the surface by the side of the discharge space of the protective film 114 (wall charge morphosis).

[0017]Then, polar voltage opposite to said discharge voltage pulse is impressed to the

transparent electrodes 103 and 104, and discharge is generated once again in discharge space. By this discharge, the accumulated electric charge (wall charge) will be removed, it will continue all over PDP, and wall charge will not exist (the process or elimination process of elimination of wall charge).

[0018]Next, the transparent electrode 103 which scans by impressing predetermined voltage to the transparent electrode 103 one by one, and is in a voltage impressing state, Wall charge is accumulated as preparation on which these luminescent cells are displayed by impressing predetermined voltage between the data electrodes 107 corresponding to luminescent cells to display among the luminescent cells belonging to this transparent electrode 103 (write-in process).

[0019]Next, image display is performed by impressing sustaining discharge pulse voltage to the transparent electrodes 103 and 104 of the whole PDP surface. Since the pressure value of this sustaining discharge pulse voltage is set up lower than the pressure value of discharge pulse voltage, in the luminescent cells which are not having wall charge formed in a write-in process, luminescence does not take place, but only the luminescent cells which performed writing discharge emit light, and image display is performed (display discharge process). About the gradation display, about 256 steps of display gradation are realized by combining serially the sustaining discharge pulse group which is about eight kinds from which the pulse number differs according to a gradation number (subfield gradation method).

[0020]Drawing 18 (a) and (b) is graph charts taking time along a horizontal axis and taking luminescence intensity and voltage along a vertical axis and in which showing the relation between impressed electromotive force and discharge delay luminescence. In PDP, since discharge is started almost all at once corresponding to a write pulse impression start as shown in drawing 18 (a) when there is no delay in discharge, i.e., the delay in luminescence, the luminescence intensity characteristic of having a very sharp peak is obtained. On the other hand, when each luminescent cells have discharge delay according to secondary electron emission efficiency, corresponding to the impression start of a write pulse, each luminescent cells start discharge scatteringly. For this reason, as shown in drawing 18 (b), compared with the case where there is no discharge delay, the peak of luminescence intensity is low and that width is large. And all luminescent cells do not start discharge all at once in this write pulse applying time. For this reason, the luminescent cells in which a contingency clause lump is not completed at the end time of impression of a write pulse, either will remain. The part shown with the dashed line in drawing 18 (b), It is an example of luminescence intensity when a write pulse is impressed for a long time than the period of the illustrated write pulse, and means that the luminescent cells which should be essentially carried out writing discharge during impression of a write pulse cannot be discharged, i.e., writing operation becomes more imperfect. In this case, when the delay in discharge is observed as luminescence of the

luminescent cells in the whole PDP surface, it is observed as a flicker of a screen display. Therefore, as shown in drawing 18 (b), when the secondary electron emission efficiency of the protective film 114 (MgO film) is falling, with highly-minute-izing and high-gradation-izing of PDP, the applying time of a write pulse will be shortened and there is a problem that the delay and writing operation of discharge become imperfect.

[0021]However, if the protective film formed by the conventional method for film deposition which uses the film deposition system shown in drawing 17 is used, the formation time of writing discharge will become long and it will be easy to generate the writing defect that discharge is not started in a prescribed period. Delay of the discharge in the display cell which serves as an isolated point in time and spatially especially is long, and, in such a case, needs to set up write-in scanning pulse width for a long time. However, when scanning pulse width is lengthened, there is a problem that the drive by dual-scan one which the number of maintenance pulses required for improvement in luminosity is restrained, and scans the upper half and lower half of a screen individually is needed. That is, in a dual-scan case, there are very many drive circuits as compared with a single scan, and it becomes the hindrance of low-cost-izing. In the conventional method for film deposition, since the crystal grain diameter is small, there is also a problem that firing potential is high.

[0022]Although a stacking tendency improves in the method for film deposition indicated to JP,9-295894,A, the orientation surface is not constant. For this reason, sputtering-proof nature may become insufficient. A crystal grain diameter becomes small and firing potential becomes high. Similarly, PDP indicated to JP,11-3665,A is not enough as the sputtering-proof nature as a protective film.

[0023]This invention was made in view of this problem, and is ****. The purpose is to provide the protective film which can raise luminosity, can reduce writing defect and can decrease a drive circuit, its method for film deposition, a plasma display panel, and a manufacturing method for the same by shortening discharge delay time, securing sputtering-proof nature.

[0024]

[Means for Solving the Problem]In a protective film which protects a dielectric layer provided in a plasma display panel from discharge, a protective film concerning this invention contains a metallic oxide, and is characterized by volume resistivity being more than 3.5×10^{11} Ω -cm.

[0025]At this time, when the number of the whole atoms is set to 100, three atoms or more of hydrogen atoms can be contained.

[0026]In a protective film which protects a dielectric layer provided in a plasma display panel from discharge, other protective films concerning this invention contain hydrogen from which the number of atoms when the number of a metallic oxide and the whole atoms is set to 100

becomes three or more.

[0027]In this invention, volume resistivity of a protective film and/or content of a hydrogen atom are specified. When having discharge delay time of writing, discharge voltage, etc. in PDP, and a close relation is found out by invention-in-this-application person and it specifies these in a suitable range about content of such volume resistivity and a hydrogen atom, Shortening of discharge delay time, a fall of discharge voltage, improvement in luminosity, etc. are attained.

[0028]Said metallic oxide may be MgO and its peak of luminescence intensity of a luminescence center at 510 thru/or 560 nm may be higher than a peak of luminescence intensity of a luminescence center at 280 thru/or 440 nm or 680 thru/or 760 nm in cathode luminescence. At this time, it is good also considering the number of said hydrogen atoms as more than the total number of deficits of the whole oxygen atom and a metal atom.

[0029]Such a protective film can be formed by heat-treating in atmosphere which contains hydrogen of excitation or an ionization state, for example.

[0030]Surface roughness Ra may be not less than 5 nm, and it is desirable to show orientation (111). (111) High sputtering-proof nature can be obtained by showing orientation.

[0031]A plasma display panel concerning this invention has one of above-mentioned protective films.

[0032]A method for film deposition of a protective film concerning this invention has a process of forming a metal oxide film, and the process of heat-treating said metal oxide film in atmosphere containing hydrogen of excitation or an ionization state.

[0033]It has the process of forming a film containing a metallic oxide, heat-treating a method for film deposition of other protective films concerning this invention in atmosphere containing hydrogen of excitation or an ionization state.

[0034]A manufacturing method of a plasma display panel concerning this invention has the process of forming a protective film by one of above-mentioned methods.

[0035]

[Embodiment of the Invention]As a result of an invention-in-this-application person's repeating an experimental study wholeheartedly that said technical problem should be solved, it found out that discharge delay time could be shortened by specifying the volume resistivity or the hydrogen content of a protective film in the predetermined range. If the orientation of a protective film is orientation (111), the best sputtering-proof nature is securable.

[0036]Hereafter, the protective film concerning this invention is explained. First, the volume resistivity and the hydrogen content of a protective film are explained.

[0037]Volume resistivity: The following relations were found out as a result of an invention-in-this-application person's considering the relation between volume resistivity and discharge delay time in more than 3.5×10^{11} ohm-cm. Drawing 1 is graph charts taking volume resistivity along a horizontal axis and taking discharge delay time along a vertical axis and in

which showing both relation.

[0038] Discharge delay time is shortened as are shown in drawing 1 and volume resistivity goes up. It depends for discharge delay time on the drive method of PDP, the shape of a discharge cell, etc. It depends for the tolerance level of discharge delay time on the number of scan lines, a drive system, etc. In PDP used when obtaining the graph shown in drawing 1, if discharge delay time will be about 4 microseconds or more, a flicker by writing defect will occur, without writing discharge occurring in the applying time of a write pulse. Since it is necessary to set up the width of a scanning pulse for a long time, it is difficult to restrict the number of maintenance pulses and to obtain sufficient luminosity. On the other hand, since the scanning pulse of width to the extent that the number of maintenance pulses is restricted is unnecessary when discharge delay time becomes 4 or less microseconds, sufficient luminosity can be obtained. Since it becomes securable [scan period sufficient with a single scan] when discharge delay time becomes 1.8 or less microseconds, a drive circuit can be reduced.

[0039] By measurement of discharge delay time, discharge delay time was measured by the display cell for ten every direction as an isolated point which actually assembles PDP and is not influenced by the discharge in other approaching display cells. The timing chart drawing 2 (a) indicates impress pulses to be, and (b) are the mimetic diagrams showing the emission spectrum obtained by discharge, and drawing 3 is a mimetic diagram showing the discharge part in measurement of discharge delay time. Discharge was simultaneously produced in the display cell 5 shown by hatching in drawing 3.

[0040] As shown in drawing 2 (a), when producing discharge, the pulse of -195V was impressed to the scanning electrode, the voltage of 70V was impressed to the data electrode, and this was performed 2000 times per display cell. As a result, as shown in drawing 2 (b), some difference arose in the emission spectrum, but time by the time when the emission spectrum fell from the time of pulse applying to 10% of peak values in the discharge which reached the peak value latest was made into the discharge delay time in this measurement.

[0041] The above tendencies obtained by such a measuring method are the same even if the shape of a drive method or a discharge cell, etc. are changed. However, the numerical value of discharge delay time changes with shape of a drive method and a discharge cell, etc.

[0042] Therefore, the volume resistivity of a protective film uses more than 3.5×10^{11} omega-cm.

[0043] Discharge delay is constituted from a standpoint of the discharge phenomenon by the sum of statistical delay and formation delay. The delay which changes with the volume resistivity of MgO among statistical delay and formation delay is only statistical delay. For this reason, even when a statistical time delay is shortened by the increase in volume resistivity, asymptotic [of the discharge delay time] is carried out to a formation time delay, and it is saturated. By PDP used when obtaining the graph shown in drawing 1, since the formation

time delay was about 1 microsecond, it is thought that the time delay more nearly statistical than drawing 1 is about 0 microsecond when volume resistivity becomes 0.4×10^{12} omega-cm. However, a statistical time delay changes also with impressed electromotive force, for example besides volume resistivity. That is, when impressed electromotive force is dropped, a statistical time delay increases. Therefore, as for volume resistivity, in order to make it possible to drive with lower impressed electromotive force, it is desirable that it is more than 0.4×10^{12} omega-cm.

[0044]The following relations were found out, as a result of an invention-in-this-application person's measuring the cathode luminescence of a MgO film and considering the relation between a luminescence center and discharge delay time. Drawing 4 is graph charts taking a luminous wavelength along a horizontal axis and taking luminescence intensity along a vertical axis and in which showing both relation. In drawing 4, a solid line shows luminescence intensity [in / dashed line / in discharge delay time / PDP for 2.0 microseconds] by discharge delay time showing the luminescence intensity in PDP for 1.2 microseconds, and the dashed dotted line shows luminescence intensity [in / in discharge delay time / PDP for 3.0 microseconds]. In each curve, luminescence intensity has a meaning in the relative value, and special semantics does not exist in the absolute value.

[0045]As shown in drawing 4, in discharge delay time, in PDP for 1.2 microseconds (solid line), the peak has appeared in luminescence intensity only in the luminous wavelength of about 520 nm.

[0046]On the other hand, in discharge delay time, in PDP for 2.0 microseconds (dashed line), a peak appears in luminescence intensity in the luminous wavelength of about 520 nm, and the luminous wavelength of about 360 nm, and the direction of the peak in the luminous wavelength which is about 360 nm is large.

[0047]In discharge delay time, in PDP for 3.0 microseconds (dashed dotted line), a peak appears in luminescence intensity in the luminous wavelength of about 400 nm, and the luminous wavelength of about 730 nm, and the direction of the peak in the luminous wavelength which is about 400 nm is large.

[0048]According to literature "M. O.Aboelfotoh:Binn.Display Res. Conf. Records. P62 (1978)." The peak which the absorption peak in the luminous wavelength of 360 thru/or 400 nm originates in an oxygen deficiency, and is called an F^+ center, the peak to which the absorption peak in the luminous wavelength of about 520 nm originates in an exciton, and the absorption peak in the luminous wavelength of about 730 nm are made into the peak resulting from excess oxygen.

[0049]Therefore, discharge delay time is considered that the defect resulting from an oxygen deficiency and excess oxygen is decreasing by a short panel. It is more desirable than this

result for the peak of the luminescence intensity of the luminescence center at 510 thru/or 560 nm to be higher than the peak of the luminescence intensity of the luminescence center at 280 thru/or 440 nm or 680 thru/or 760 nm in cathode luminescence. At this time, it is thought that the number of the hydrogen atoms in a protective film is contained as for more than the total number of deficits of the oxygen atom in a protective film and a metal atom.

[0050]Cathode luminescence (CL) is analytical skills which detect luminescence as the energy relaxation process when a sample is irradiated with an electron beam, and acquire information, including the defect in a sample, etc. In cathode luminescence here, after assembling PDP once and measuring the discharge delay time by the above-mentioned method, PDP was decomposed, the protective film was directly irradiated with the electron beam, and the luminescence was detected.

[0051]Next, how to manufacture the protective film possessing the above volume resistivity is explained. Drawing 5 is a mimetic diagram showing the 1st film deposition system used for manufacture of a protective film.

[0052]The vacuum evaporation chamber 11 and the hydrogen treatment chamber 12 which were divided with the partition bulb 13 are provided in the 1st film deposition system.

[0053]The substrate 14a with which a dielectric film etc. are already formed and a MgO film is formed is attached to the upper part of the vacuum evaporation chamber 11. The deposition source 15 which consists of MgO(s) as a raw material of a protective film is attached to the lower part of the vacuum evaporation chamber 11. The gas inlet the heater 22 which heats the substrate 14a, and for O₂ gas (not shown) is established in the vacuum evaporation chamber 11.

[0054]On the other hand, the substrate 14b with which the MgO film was formed is attached to the upper part of the hydrogen treatment chamber 12. The heater 17 which heats the inside of the heater 16 which heats the substrate 14b, and the chamber 12 is allocated by the hydrogen treatment chamber 12. In the lower part of the hydrogen treatment chamber 12, the electrodes 18 and 19 connected to external RF generator (RF) 20 are arranged, and the discharge 21 occurs among these electrodes 18 and 19. The gas inlet for Ar gas and H₂ gas (not shown) is established in the hydrogen treatment chamber 12.

[0055]When manufacturing a protective film using the 1st film deposition system constituted in this way, the substrate 14a is first fixed to the upper part of the vacuum evaporation chamber 11. Subsequently, the substrate 14a is heated, for example at 230-270 °C with the heater 22, and the inside of the vacuum evaporation chamber 11 is exhausted until a degree of vacuum reaches abbreviation 8×10^{-4} Pa. Next, by irradiating the deposition source 15 with the electron beam 23, introducing oxygen gas in the vacuum evaporation chamber 11 by 30-80-ml the flow for / (normal condition), in order to arrange the crystal orientation of a MgO film, A 5000 thru/or

10000-A MgO film is formed on the field which counters the deposition source 15 of the substrate 14a. And the partition bulb 13 is opened and the substrate 14b with which the MgO film was formed is moved into the hydrogen treatment chamber 12.

[0056]Then, in the hydrogen treatment chamber 12, the inside of the substrate 14b and the hydrogen treatment chamber 12 is heated, for example at 230-270 °C with the heaters 16 and 17, respectively. The inside of the hydrogen treatment chamber 12 is exhausted until a degree of vacuum is set to abbreviation 5×10^{-4} - 9×10^{-4} Pa. After a degree of vacuum reaches abbreviation 5×10^{-4} - 9×10^{-4} Pa, argon gas is introduced regulating the pressure so that a degree of vacuum may be set to 2.1×10^{-1} Pa. Subsequently, introducing hydrogen gas by 30-80-ml the flow for (normal condition), by RF generator 20, 13.56-MHz high frequency is impressed to the electrodes 18 and 19, for example, and the discharge 21 is generated in the hydrogen treatment chamber 12. And hydrogen treatment of a MgO film is performed by exciting a hydrogen atom by the discharge 21, generating plasma, and putting to the hydrogen which excited the MgO film currently formed at the substrate 14b, for example for 8 to 12 minutes.

[0057]Drawing 6 is a mimetic diagram showing the 2nd film deposition system used for manufacture of a protective film.

[0058]The vacuum evaporation chamber 11 and the hydrogen treatment chamber 12a which were divided also into the 2nd film deposition system with the partition bulb 13 are provided. Since the structure of the vacuum evaporation chamber 11 is the same as that of the thing of the 1st film deposition system, the detailed explanation is omitted.

[0059]The generating means of the plasma of RF generator 20 grade is not provided in the hydrogen treatment chamber 12a, instead the generating means of the hydrogen ion is provided in it. Specifically, the ion gun 26 which turns ion to the substrate 14b and irradiates with it in the hydrogen treatment chamber 12a is formed. The ion gun 26 is connected with the hydrogen cylinder 25 via the flow regulator (MFC:Mass Flow Controller) 24 formed in the exterior of the hydrogen treatment chamber 12a.

[0060]When manufacturing a protective film using the 2nd film deposition system constituted in this way, a MgO film is formed like the case where the 1st film deposition system is used, and the substrate 14b with which the MgO film was formed is moved into the hydrogen treatment chamber 12.

[0061]Then, in the hydrogen treatment chamber 12, the inside of the substrate 14b and the hydrogen treatment chamber 12 is heated, for example at 230-270 °C with the heaters 16 and 17, respectively. After it exhausts the inside of the hydrogen treatment chamber 12 and a degree of vacuum reaches abbreviation 8×10^{-4} Pa, hydrogen treatment of a MgO film is performed by irradiating with a hydrogen ion the MgO film in which membranes are formed by

the substrate 14b from the ion gun 26. The flow of hydrogen was considered as a part for 20-100-ml/.

[0062]Drawing 7 is a mimetic diagram showing the 3rd film deposition system used for manufacture of a protective film.

[0063]The 3rd film deposition system has the structure by which the hydrogen treatment chamber 12a was united with the vacuum evaporation chamber 11 in the 2nd film deposition system.

[0064]That is, the hydrogen treatment chamber 12a is not formed, but the heater 17 and the ion gun 26 are formed in the vacuum evaporation chamber 11.

[0065]When a protective film is manufactured using the 3rd film deposition system constituted in this way, For example, the inside of the substrate 14a and the vacuum evaporation chamber 11 is heated at 200 thru/or 270 °C with the heaters 22 and 17, respectively, A MgO film is formed, for example at 80A/second in speed by setting a degree of vacuum to 2.7×10^{-2} Pa, introducing oxygen gas and hydrogen gas by 35 thru/or 70-ml the flow for part (normal condition) 10 thru/or 30-ml/(normal condition) for /, respectively, and irradiating the deposition source 15 with the electron beam 23. Hydrogen treatment of a MgO film is performed by irradiating with a hydrogen ion the MgO film which can come, simultaneously is formed from the ion gun 26 at the substrate 14b. The flow of hydrogen at this time is a part for 20-100-ml/.

[0066]Hydrogen content: The following relations were found out as a result of a three-atom or more invention-in-this-application person's considering the relation between a hydrogen content and discharge delay time, when the number of the atoms of the whole protective film is set to 100. Drawing 8 is graph charts taking a hydrogen content (the number of hydrogen atoms when the number of the atoms of the whole protective film is set to 100) along a horizontal axis, and taking discharge delay time along a vertical axis and in which showing both relation.

[0067]Discharge delay time is shortened as are shown in drawing 8 and a hydrogen content rises. It depends for discharge delay time on the drive method of PDP, the shape of a discharge cell, etc. as mentioned above. It depends for the tolerance level of discharge delay time on the number of scan lines, and a drive method. In PDP used when obtaining the graph shown in drawing 8, when discharge delay time will be about 1.8 microseconds or more, dual-scan one of PDP is needed for reservation of a scan period. Since it is necessary to set up the width of a scanning pulse for a long time, it is difficult to restrict the number of maintenance pulses and to obtain sufficient luminosity. On the other hand, since reservation of scan period sufficient with a single scan is possible in discharge delay time being less than 41.8 seconds, a drive circuit can be reduced. Since the scanning pulse of width to the extent that the number of maintenance pulses is restricted is unnecessary, sufficient luminosity can be obtained.

[0068]The invention-in-this-application person found out the following relations about the

thru/or 1, substrate temperature shall be 150 thru/or 250 **, an evaporation rate is considered as a part for 1000 thru/or -2000A/and a 5000 thru/or 15000-A protective film is formed, The hydrogen content of the protective film will be 3 thru/or 10 atoms, when the number of the atoms of the whole protective film is set to 100, and the surface roughness Ra is set to not less than 5 nm.

[0076]In order to change only the division ratio of hydrogen and oxygen and to investigate the influence on a hydrogen content under conditions, such as a pressure in the above chambers, Signal height is measured by the ERDA (Elastic Recoil Detection Analysis) method about the number of H atoms which exist in a protective film, Signal height was measured by the RBS (Rutherford Back-scattering Spectrum) method about the number of Mg atom and O atoms. The ERDA method makes a detection angle the angle inclined 20 degrees to the incident beam axis to the detection angle in the RBS method being an angle inclined 140 degrees to the incident beam axis. In order similarly to change the rate of the number of hydrogen atoms to the number of oxygen atoms and to investigate the influence of surface roughness Ra on a protective film, surface roughness Ra was measured using the atomic force microscope (AFM:AtomicForceMicroscopy).

[0077]Drawing 10 is a figure showing the spectrum of H atom at the time of setting the division ratio of hydrogen and oxygen in the atmosphere in a chamber to 0.5, and Mg atom, and the graph charts in which (a) shows the spectrum of H atom, and (b) are graph charts showing the spectrum of Mg atom. Drawing 11 is a figure showing the spectrum of H atom at the time of setting the division ratio of hydrogen and oxygen in the atmosphere in a chamber to 0.2, and Mg atom, and the graph charts in which (a) shows the spectrum of H atom, and (b) are graph charts showing the spectrum of Mg atom.

[0078]When the division ratio of hydrogen and oxygen was set to 0.5, as shown in drawing 10 (a) and (b), as for the signal height of H atom, the signal height of 39 and Mg atom was set to 2810. Therefore, the ratio of H/Mg in the protective film in the atomic number in this case is set to 0.13. On the other hand, when the division ratio of hydrogen and oxygen was set to 0.2, as shown in drawing 11 (a) and (b), as for the signal height of H atom, the signal height of 19 and Mg atom was set to 3190. Therefore, the ratio of H/Mg in the protective film in the atomic number in this case is set to 0.05.

[0079]According to the result separately measured by the RBS method, the ratio of O/Mg in the protective film in an atomic number when the ratio of O/Mg in the protective film in the atomic number at the time of setting the division ratio of hydrogen and oxygen to 0.5 sets the division ratio of 1.20, hydrogen, and oxygen to 0.2 was 1.02.

[0080]From these results, the hydrogen content of the protective film at the time of setting the division ratio of hydrogen and oxygen to 0.5 is set to 5.6 when the number of the atoms of the whole protective film is set to 100, and it at the time of setting the division ratio of hydrogen

and oxygen to 0.2 is set to 2.4.

[0081]Drawing 12 is a microphotograph in which the shape of surface type of the protective film at the time of setting the division ratio of hydrogen and oxygen in the atmosphere in a chamber to 0.5 is shown, and drawing 13 is a microphotograph in which the shape of surface type of the protective film at the time of setting the division ratio of hydrogen and oxygen in the atmosphere in a chamber to 0.2 is shown.

[0082]As a result of measuring surface roughness Ra of a protective film using an atomic force microscope, when the division ratio of hydrogen and oxygen in the atmosphere in a chamber is set to 0.5, Ra = it was 5.43 nm, and it was Ra=4.97nm when the division ratio of hydrogen and oxygen in the atmosphere in a chamber was set to 0.2.

[0083]Drawing 14 is a figure showing the result of the X diffraction at the time of setting the division ratio of hydrogen and oxygen in the atmosphere in a chamber to 0.5, and drawing 15 is a figure showing the result of the X diffraction at the time of setting the division ratio of hydrogen and oxygen in the atmosphere in a chamber to 0.2.

[0084]Even if it is which case, according to the X diffraction (XRD:X-Ray Diffraction), it can be said that the protective film has orientation (111). (111) Orientation is the stacking tendency of the single crystal of MgO, a secondary electron emission factor is large and it is known widely that it is the stacking tendency excellent in sputtering-proof nature. Therefore, the film which has orientation (111) is preferred as a protective film of PDP.

[0085]What is necessary is to introduce oxygen gas, and a steam or hydrogen gas in a chamber, and just to control a division ratio, in order to obtain the division ratio of hydrogen of 0.3 thru/or 1, and oxygen. Since hydrogen and oxygen dissociate in a steam by the plasma generated by the electron beam when a steam is introduced, it becomes possible to control a division ratio.

[0086]When forming a protective film, parts, such as a career which conveys a substrate between the inside of a film deposition system and the exterior, are used. On the surface of these parts, a MgO film 0.1 thru/or 1 mm thick may be formed beforehand, for example. Since the MgO film formed at this part absorbs moisture when taken out to the exterior of a chamber, if put in in a chamber with that back substrate, it can distribute a steam in a chamber. Therefore, the division ratio of hydrogen in a chamber and oxygen is controllable by flowing oxygen gas from the exterior.

[0087]

[Effect of the Invention]Since the content of the volume resistivity which has discharge delay time of writing, discharge voltage, etc. in PDP, and a close relation, and a hydrogen atom is appropriately specified according to this invention as explained in full detail above, discharge delay time can be shortened. As a result, luminosity can be raised, generating of writing defect can be prevented, and the number of drive circuits can be reduced and cost can be reduced.

Driver voltage (discharge voltage) can be reduced and power consumption can also be reduced.

[Translation done.]

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Attachment to Response
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